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Crystal structure and conductivity of bismuth-containing complex oxides

In the paper, a comprehensive systematic study of different classes of bismuth containing oxide compounds was carried out. The relationship between composition, temperature and concentration regions of existence of stable, specific structure and properties of solid solutions on the basis of vanadates, molybdates, niobates and bismuth was found. The general regularities of synthesis of solid solutions with different variants of solid-phase and soluble methods were determined. On this basis, the optimal conditions for obtaining single-phase materials were formulated. For the first time the temperature and concentration boundaries of the regions of homogeneity and areas of stable existence of polymorphic modifications of solid solutions were defined and/or refined. The structural parameters of the synthesized phases were determined. By the method of electrochemical impedance spectroscopy the nature and features of impedance spectra, the temperature and concentration dependences of electrical conductivity of ceramic materials based on bismuth containing complex oxides were identified.

Key words: method of electrochemical impedance spectroscopy; bismuth containing oxides; oxygen-ionic conductivity; thermocycling.

Introduction

The complex oxides on the basis of Bi_2O_3 provide a vast class of objects of interest from the point of view of both fundamental and applied science. Among practically important physical and chemical properties can distinguish oxygen-ion

and mixed conductivity in middle temperature region (300–700 °C), ferroelectric and magnetic effects. Bismuth-containing compounds crystallize in different structure types to a greater extent crystal – or perovskite-like, including having a layered structure. Depending on the dimensionality of charge transfer process, the bismuth-containing complex oxides can be divided into 3 types: three-dimensional (family of complex oxides that is similar to δ-Bi_2O_3); two-dimensional (BIMEVOX family); and one-dimensional, represented by phases on the basis of $Bi_{26}Mo_{10}O_{69}$, containing column $[Bi_{12}O_{14}]_\infty$. An important feature of the compounds is the presence of the cation of bismuth $6s^2$ lone-pair electrons, which leads to a high polarizability of the cationic sublattice. The stereochemical activity of the electron pair of bismuth ions is manifested in the ability to the formation of highly disordered oxygen environment of bismuth, change in symmetry of the coordination polyhedras and the way to ensure the dissociation of oxygen molecules.

This work presents the results of studies of bismuth-containing complex oxide compounds of different structural families, held at the Ural University in recent years.

The experimental part

The series compounds of $Bi_4V_{2-x}Me_xO_{11-\delta}$ or BIMEVOX (Me=Cu, Fe, Ti, Nb), $Bi_{13}Mo_{5-x}Me_xO_{34-\delta}$ and $Bi_{13-x}Me_xMo_5O_{34\pm\delta}$, (Me=Mg, Ca, Sr, Ba, Co, Fe), $Bi_{6.95}Y_{0.05}Nb_{2-y}Me_yO_{15,5\pm\delta}$ and $Bi_3Nb_{1-y}Me_yO_{7\pm\delta}$ (Me=Fe, Zr, W) were obtained by standard ceramic technology, or using different variants of synthesis of the mortar. The features of synthesis for each particular case are described in [1–15].

X-ray examination of samples was carried out using diffractometer DRON-3 (CuKα-radiation, monochromator of pyrolytic graphite on the reflected beam), D8 ADVANCE (CuKα-radiation, β-filter, position sensitive detector VÅNTEC, high-temperature chamber Anton Paar HTK 1200N). Analysis of the phase composition and calculation of the crystallographic parameters was carried out using DIFFRAC^{plus} EVA, Match-DEMO, Celref and databases PDF4+ ICDD, COD and AMCSD. Dilatometric analysis was performed using the dilatometer DIL 402 C Netzsch with a vacuum-tight oven, differential thermal analysis was performed using thermoanalyzer STA 409 PC Luxx, Netzsch. Microscopic investigations were performed using scanning electronic (raster) microscope JEOL JSM 6390LA consoles and energy dispersive JEOL JED 2300. Elemental analysis of samples was performed by atomic emission spectroscopy with inductively coupled plasma and atomic absorption spectrometry on the spectrometer iCAP 6500 and M6 Solar Thermo Scientific. The total conductivity of the samples was measured by the method of impedance spectroscopy (impedancemetry Z-350M, Z-3000 firm "Elins").

Results and discussion

For all systems the processes of phase formation during their synthesis using a solid-phase, different versions of mortar methods, mechano-chemical activation were systematically investigated, the optimum conditions for obtaining single-

phase compositions were found. The phase formation in the systems Bi_2O_3-V_2O_5-oxides Cu, Fe, Ti, Nb is always in some series-parallel stages with formation of intermediate products of composition $Bi_{1.33}V_2O_6$ and $BiVO_4$, vanadates of the respective metals, for example, $Cu_5V_2O_{10}$, $Fe_2V_4O_{13}$, mixed oxides of bismuth and related cations ($Bi_{24}Ti_2O_{40}$, $Bi_{20}TiO_{32}$, $Bi_8Nb_{18}O_{57}$). It is established that the oxides of bismuth cations and the relevant cations the processes of formation of phases BIMEVOX in the synthesis using liquid precursors is generally similar to the processes of phase formation during solid-phase synthesis. The vanadate bismuth of the composition $BiVO_4$ is formed in all methods in the primary sludge. The interaction of the bismuth components with the formation of single-phase product in the field homogeneity during the synthesis phases BIMEVOX using liquid precursors ends at temperatures 100–150 K lower than during solid-phase synthesis. When using the mechano-chemical method, the samples composition $Bi_4V_2O_{11}$, $Bi_4V_{1.7}Cu_{0.15}Ti_{0.15}O_{11-\delta}$, $Bi_4V_{1.8}Fe_{0.2}O_{11-\delta}$ were obtained only after annealing of the mechanically activated mixture at a temperature of 873 K. Under the same conditions of mechano-chemical synthesis of single-phase $Bi_4V_{1.4}Nb_{0.6}O_{11-\delta}$ was obtained after two minutes of activation. The phase formation by mechanical activation, as with other methods of synthesis goes through several series-parallel stages, which confirms the general complex nature of the interaction in the layered perovskite-like systems. However, at the final stage of the synthesis by any of the proposed options with appropriate concentrations of metal formed solid solutions belong to one of the possible polymorphic modifications of bismuth vanadate are formed [1–5].

The formation of solid solutions based on bismuth molybdate $Bi_{13}Mo_5O_{34\pm\delta}$ during the synthesis of solid-phase method goes through the stage of formation of intermediate compounds $Bi_{38}Mo_7O_{78}$ and Bi_2MoO_6; complex oxides of bismuth and a metal dopant. In the synthesis using soluble reagents as impurities has a significant amount of α–phase ($Bi_2Mo_3O_{12}$), a hydroxide of bismuth, Bi_2MoO_6. Analysis of reaction products after different stages of thermal processing has shown that in the case of the introduction in the process of synthesis procedures for the tempering of samples, the number and concentration of intermediates is significantly reduced, and single-phase final product forms at a temperature 1073–1123 K. The structural features of the different structural families of complex oxides are investigated, the boundaries of the regions of homogeneity, structural parameters and concentration intervals of existence of polymorphic modifications are defined. The high-symmetry complex oxides are formed on the basis of δ-Bi_2O_3 with the fluorite structure with the occupancy of the oxygen sublattice at about 75 % (PR. gr. *Fm*-3*m*) with partial substitution of metal ions for other cations. In this case, the region of homogeneity of solid solutions has a small length, for example, for a series $Bi_3Nb_{1-y}Zr_yO_{7\pm\delta}$ is the boundary located at $x = 0.4$, the series $Bi_{6.95}Y_{0.05}Nb_{2-y}Zr_yO_{15.5\pm\delta}$ when $y = 0.3$. For $Bi_{6.95}Y_{0.05}Nb_{2-y}Fe_yO_{15.5\pm\delta}$ at a maximum temperature of 1073 K synthesis it is limited by the composition $y = 0.2$.

Outside the homogeneity region, or when the temperature changes often there is a mixture of two phases pseudokoningii

type Bi_3NbO_7 with close lattice parameters and different content of metals. At low concentrations of dopant the stabilization of the tetragonal modification of solid solutions is possible, for example, for $Bi_3Nb_{1-y}W_yO_{7\pm\delta}$ or $Bi_3Nb_{1-y}Fe_yO_{7\pm\delta}$ ($y = 0.1$).

The existence regions of structural modifications phases BIMEVOX vary depending on the composition and less – used method of synthesis. With a small content of operauser metal the solid solutions crystallize in the monoclinic (Pr. gr. *C*2/*m*) or orthorhombic ((Pr. gr. *Aba*2 или *Amam*) modification, by increasing the concentration of the dopant leads to the formation of tetragonal γ-modification. In the wide concentration interval of the tetragonal γ-modification (Pr. gr *I*4/*mmm*) at room temperature is stable due to the substitution positions of vanadium to niobium ($0.30 \le x \le 0.90$), iron ($0.20 \le x \le 0.50$) and with a double substitution of iron and niobium ($0.2 < x < 0.575$). γ-modification BICUTIVOX at room temperature was obtained for compositions with $0.25 \le x \le 0.50$ only during rapid cooling (tempering) with the last stage of synthesis. The series of solid substitution solutions based on bismuth molybdate $Bi_{13}Mo_5O_{34\pm\delta}$ crystallize in triclinic and monoclinic modifications. In particular, the triclinic modification of (Pr. gr. *P*-1) forms by substitution in the sublattice of molybdenum and low concentrations of dopant for the series $Bi_{13}Mo_{5-y}Co_yO_{34\pm\delta}$ ($y \le 0.05$) or bismuth for $Bi_{13-x}Mg_xMo_5O_{34\pm\delta}$ ($x \le 0.1$), $Bi_{13-x}Ca(Sr, Ba)_xMo_5O_{34\pm\delta}$ ($x \le 0.4$), $Bi_{13-x}Co_xMo_5O_{34\pm\delta}$ ($x \le 0.05$). Monoclinic modification (Pr. gr. P2/*c*) forms with the substitution in the sublattice of molybdenum compounds for $Bi_{13}Mo_{5-y}Co_yO_{34\pm\delta}$ ($y \le 0.2$) or bismuth, for example, $Bi_{13-x}Mg_xMo_5O_{34\pm\delta}$ ($x \le 0.4$), $Bi_{13-x}Ca(Sr, Ba)_xMo_5O_{34\pm\delta}$, ($x \le 0.7$), $Bi_{13-x}Co_xMo_5O_{34\pm\delta}$ ($x \le 0.2$). An x-ray when you change the symmetry of the unit cell for different structural types is shown in Fig. 1, an example of the dependence of unit cell parameters from the structure is shown in Fig. 2.

The regularities of the change of symmetry and the unit cell parameters of different polymorphic modifications of investigated series of samples depending on

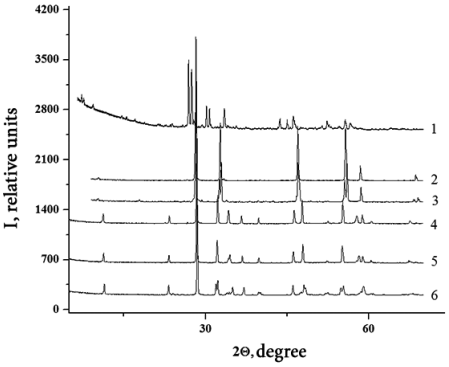

Fig. 1. Examples of radiographs of different structural types: : 1 – $Bi_{12.9}Ba_{0.1}Mo_5O_{34\pm\delta}$, (Pr. gr. *P*-1), 2 – $Bi_3Nb_{0.8}W_{0.2}O_{7\pm\delta}$, (Pr. gr. *Fm*–3*m*); 3 – $Bi_3Nb_{0.9}Fe_{0.1}O_{7\pm\delta}$, (Pr. gr. *I*-4*m*2); 4 – γ-BIMEVOX (Pr. gr. *I*4/*mmm*); 5 – β-BIMEVOX (Pr. gr. *Amam*), 6 – α-BIMEVOX (Pr. gr. *C*2/*m*)

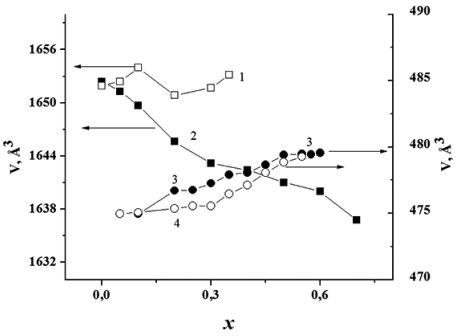

Fig. 2. The dependence of the volume of the unit cell composition: 1 – $Bi_{13}Mo_{5-y}Fe_yO_{34\pm\delta}$; 2 – $Bi_{13-x}Ca_xMo_5O_{34\pm\delta}$; 3 – $Bi_4V_{2-x}Fe_{x/2}Nb_{x/2}O_{11-\delta}$; 4 – $Bi_4V_{2-x}Fe_xO_{11-\delta}$

temperature were revealed. For example, for phases BIMEVOX family with increasing content of the dopant extends the temperature region of existence of the tetragonal γ-modification. The effect of the uneven change of parameters while maintaining the linearity of the change of unit cell volume with temperature for a series BICRFEVOX is found that is explained changes in vanadate layer structure.

The study of the crystal structure of tetragonal $Bi_4V_{2-x}Fe_xO_{11-\delta}$ depending on temperature and oxygen partial pressure revealed a significant stability of this modification in a fairly wide range of thermodynamic parameters. The change in the structure of the tetragonal modification BIFEVOX in orthorhombic occurs in an environment with low oxygen content (at $lgPo_2 = -18.0$ (atm.)) and at temperatures above 770 K. The baric dependences of the volume of the unit cell $Bi_4V_{1.7}Fe_{0.3}O_{11-\delta}$ at different temperatures are shown in Fig.3. In addition, the samples of this series with x = 0.3–0.4 have the greatest stability under thermal cycling.

Using high-temperature x-ray studied the thermal behavior of the series $Bi_{13}Mo_{5-x}Me_xO_{34-\delta}$ and $Bi_{13-x}Me_xMo_5O_{34\pm\delta}$ with different dopants was studied. The changes of unit cell parameters in the phase transition from triclinic to monoclinic modification occurs abruptly and is accompanied by a small contraction of the unit cell. In the areas above and below the transition temperature the dependence is linear. However, at temperatures above 950 K there is a slight deviation from the linear behavior. An example of such dependencies for $Bi_{13}Mo_{4.9}Fe_{0.1}O_{34\pm\delta}$, obtained according to x-ray and neutron diffraction, are given in fig. 4. Most likely this is due to the change in the mechanism of interaction between columnar elements and/or disordered polyhedra of molybdenum-oxygen framework of the same symmetry.

With the increase in the concentration of the dopant the transition temperature from monoclinic to triclinic modification expected decreases: for example, with the composition $Bi_{12.9}Ca_{0.1}Mo_5O_{34\pm\delta}$ the phase transition temperature was equal to ~593 K, for the composition $Bi_{12.6}Ca_{0.4}Mo_5O_{34\pm\delta}$ ~523 K.

The evaluation of the elemental composition of the investigated phases, taken in powder, or near the surface and in the

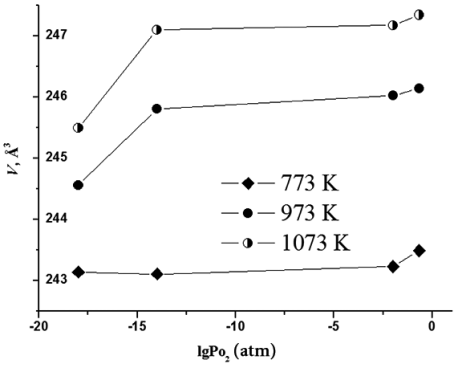

Fig. 3. The baric dependence of the volume of the unit cell $Bi_4V_{1.7}Fe_{0.3}O_{11-\delta}$ at different temperatures

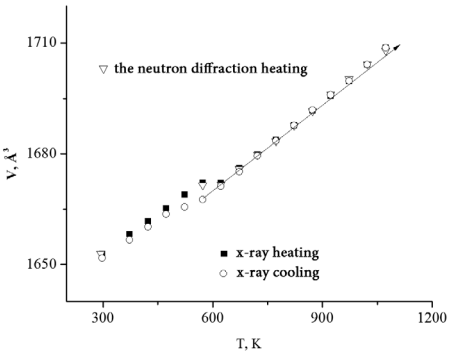

Fig. 4. The dependence of the volume of the unit cell $Bi_{13}Mo_{4.9}Fe_{0.1}O_{34\pm\delta}$ on temperature according to neutron and x-ray diffraction. The arrow shows a linear plot

bulk sintered pellets by atomic spectroscopy, and electron microscopy revealed that is not always realized even distribution of atoms in the structures of the solid solutions. This necessitates not only the phase, but the element of local and general control elements content in them. For example, for the system BICUTIVOX regardless of the method of synthesis has been uneven joining of titanium atoms into the crystal lattice of the solid solution accompanied by the formation of uncontrolled trace impurities phases, enriched with titanium, which affects mechanical and electrical properties. Such effect is absent for BIFEVOX, BINBVOX. The uniform distribution of atoms in the structure is observed for all columnar series of molybdates of bismuth. For bismuth niobates with increasing concentration of the dopant is observed the formation of two structures pseudokoningii (let's denote them as δ and δ/). For example, by the results of surface analysis and sample volume $Bi_{6.95}Y_{0.05}Nb_{1.4}Zr_{0.6}O_{15.5\pm\delta}$ single-phase slightly is saturated with bismuth, and the other is saturated with niobium. The composition of one phase is δ- $Bi_3Nb_{0.72}Zr_{0.28}O_{7-\delta}$, and the second is δ/-$Bi_{1.7}Nb_{0.23}Zr_{0.07}O_{3.30-\delta}$. The coefficients of thermal expansion of both phases are close, the only difference between them is in the area 973–1073 K, where the phase δ/ is observed an anomaly of the unit cell parameters associated with the beginning of the collapse. According to the RFA above 973 K we observe the emergence of phase $Bi_{12}Nb_{0.29}O_{18.7+x}$ and a simultaneous decrease of the intensities of the reflexes of the phase δ/.

For all series of samples the processes of non-isothermal sintering of ceramic briquettes were investigated that are allowed to establish their characteristics and the optimal values of the temperature-time characteristics of sintering. The samples were characterized by density, sintering, porosity, values of linear coefficients of thermal expansion. The highest value for LCTR phases BIMEVOX is ~20×10^{-6} K^{-1} and is characteristic of high-temperature γ-modification at low concentrations of dopant. For columnar of molybdates of bismuth it is a bit lower, $14–16\times10^{-6}$ K^{-1}. Thus, unlike phases BIMEVOX , size LCTR for triclinic and monoclinic modifications are close, therefore, a sharp change in their volume during the phase transition does not occur, which is beneficial to the mechanical properties of the ceramic briquettes. The average values for LCTR bismuth niobates are in the area of $11.7\times10^{-6} – 11.8\times10^{-6}$ K^{-1}.

By the method of electrochemical impedance spectroscopy identified the nature and features of impedance spectra, the temperature and concentration dependences of electrical conductivity of ceramic materials of all investigated series of samples were identified. The hodographs of the impedance of the studied compounds have the typical form of polycrystalline ionic conductors, and are composed of two or more combined semicircles, corresponding to the total resistance of the sample, the electrode and diffusion processes. The example of impedance diagram is shown in Fig. 5. The corresponding equivalent circuit is based on a block-layered model that includes as mandatory elements of the impedance and the frequency-dependent component (examples in Fig. 6).

The course of temperature dependences of electrical conductivity is consistent with the concentration intervals of exis-

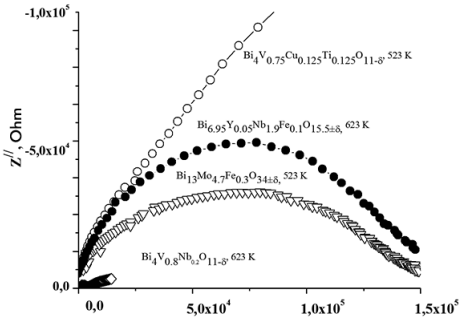

Fig. 5. Impedance diagrams for different compounds

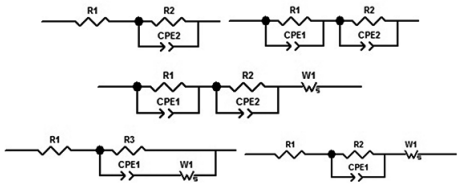

Fig. 6. Examples of equivalent circuits used for analysis of impedance

tence of structural modifications: in the presence of phase transitions within the interval on politermo reflect the changes in the slope of the dependencie. For example, for phases BIMEVOX at low concentrations of dopant (for example, x = 0.05), typical observed γ→β (853 K) and β→α (723 K) of successive phase transitions corresponding to the change of structure (I4/mmm → Amam → C2/m) and is characterized by the change of activation energy of conductivity of solid solutions. For γ-modification phases BIMEVOX solid solutions the values of activation energies at high temperatures are characteristic of the magnitude of 0.2–0.4 eV. The transition into an ordered γ/-modification with decreasing temperature is accompanied by a change of the tilt according to lgσ – 10^3/T and the increase of the activation energy to 0.5–0.7 eV. The electrical conductivity of ceramics made from powders obtained by the methods of synthesis using liquid precursors, is in average by 0.5 orders of magnitude higher compared with ceramics of the same composition obtained by a solid phase method. Investigation of electrical conductivity of some compositions of the solid solution BIFEVOX, BINBVOX depending on the partial pressure of oxygen showed that this dependence has a linear character, indicating a predominant oxygen-ion conductivity of this type of solid solutions.

On the temperature dependence of conductivity of solid solutions on the basis of $Bi_{13}Mo_5O_{34\pm\delta}$ are dedicated three ranges, characterized by different values of activation energy of conductivity: low-temperature is inherent triclinic form $E_{акт}$ (HT) = 0.9–1.3 eV; medium- and high-temperature (($E_{акт}$ (BT) = 0.5–0.6 эВ; $E_{акт}$ (CT) = 0.65–0.8 эВ is inherent to the monoclinic form. On the example of the samples of molybdates of bismuth-doped iron it is shown that the change in conductivity of materials in high-temperature and medium-temperature interval is correlated with changes in the oxygen sublattice of compounds within the life of the monoclinic modification, namely, due to the disordering of the oxygen polyhedra and the emergence of structure in the solid solution of the conjugate Mo-O of trigonal bipyramid.

For bismuth niobates the temperature dependence of electrical conductivity are linear, as determined by the absence of phase transitions in solid solutions of these compounds. The value of activation energy of conductivity is an average value of 0.9–1.1 eV. The highest conductivity have samples with a high concentration of phase δ/, which is a solid solution based on the highly conductive δ-modification

of bismuth oxide. Examples of the dependences are shown in Fig. 7.

The dependence of the conductivity on the concentration of the dopant usually has a parabolic type with a maximum at small concentrations of the dopant, which

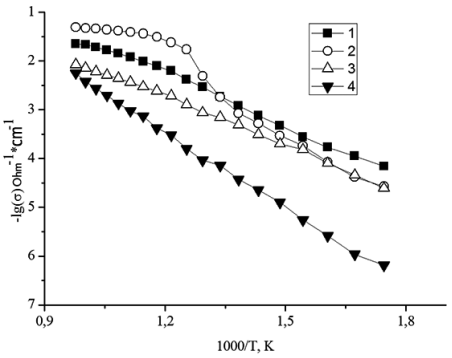

Fig. 7. Temperature dependence of conductivity of complex oxides: 1 – $Bi_4V_{1.75}Fe_{0.125}Nb_{0.125}O_{11-\delta}$; 2 – $Bi_4V_{1.9}Fe_{0.1}O_{11-\delta}$; 3 – $Bi_{12.8}Ba_{0.2}Mo_5O_{34\pm\delta}$; 4 – $Bi_{6.95}Y_{0.05}Nb_{1.7}Fe_{0.3}O_{15.5\pm\delta}$

is typical for many oxide systems (Fig. 8) and can be determined by the interaction of defects, or any structural factors. For example, the columnar bismuth molybdates the maximum value of conductivity is typical for the «transition state»: the area of occurrence of monoclinic or triclinic modifications modifications in the parameters is close to monoclinic.

According to the results of the executed complex studies you can identify the most promising formulations from the viewpoint of conductive properties and stability under conditions of operation at elevated temperatures and variation of

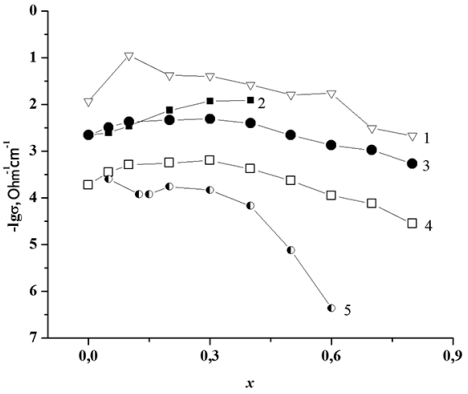

Fig. 8. The dependence of the conductivity of complex oxides on: 1 – BINBVOX, 1023 K; 2 – $Bi_{13}Mo_{5-y}Fe_yO_{34\pm\delta}$; 1023 K; 3 – $Bi_{13-x}Ca_xMo_5O_{34\pm\delta}$, 1023 K; 4 – $Bi_{13-x}Ca_xMo_5O_{34\pm\delta}$, 723 K; 5 – BIFEVOX, 673 K

thermodynamic parameters. It is series of solid solutions BIFEVOX, BINBVOX, BIFENBVOX with a dopant concentration of 25–30 mol. % substituted columnar bismuth molybdate compositions $Bi_{12.8}Ba_{0.2}Mo_5O_{34\pm\delta}$ и $Bi_{13}Mo_{4.7}Fe_{0.3}O_{34\pm\delta}$.

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